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(54) POLYMER ARTICLE WITH SLIPPERY SURFACE

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of surfaces of solid polymeric articles to modify surface properties thereof, such as coefficient of friction. In another aspect, it relates to normally hydrophobic shaped articles of polymers which have been chemically treated to form hydrophilic surfaces. In another aspect, it relates to body insertion devices or instruments, such as enema nozzles, useful for medical examination, diagnostic, or therapeutic purposes. In a further aspect, it relates to shaped articles of copolymers of styrene with other vinyl comonomers such as acrylonitrile, at least one surface of which has been treated to render the same hydrophilic and slippery when wet with water.

It is well known that many polymer surfaces are strongly hydrophobic and have relatively high coefficients of friction. These properties somewhat limit the application of shaped articles made from such polymers. For example, medical and therapeutical devices used for examination, diagnostic, or therapeutic purposes fabricated from such polymers, as well as metals such as stainless steel, when inserted into a body cavity or orifice often cause discomfort or pain when inserted, due to the relatively high coefficient of friction of the surfaces of such devices. It is usual, in order to overcome such problems, to apply a lubricant, such as petroleum jelly or other lubricants of paraffinic base or water-soluble gum base, to the surface of the device to aid its insertion (for example see U.S. Patent No. 2,869,545). However, application of a lubricant does not always satisfactorily overcome the problems mentioned, or it raises other problems. The lubricant is often wiped off or dislodged from the surface to which it is applied upon insertion of the lubricated device into the body orifice. Often the lubricant is incorrectly or inadequately applied to the surface. The lubricant may not, in fact, provide the desired or required degree of lubricity in contact with body membranes or tissues. The body orifice or cavity may become in effect undesirably contaminated by the lubricant or the sample withdrawn for clinical testing may be contaminated with the lubricant. The need for a sterile lubricant, or maintaining lubricant sterile during storage, is a significant cost, and in general the handling of and requirement for lubricant is bothersome.

Representative of art describing various treatments of various polymer materials to modify surface properties thereof is U.S. Patent No. 2,400,720 (Staudinger et al), which discloses treating polystyrene with a sulfonating agent, such as fuming sulfuric acid, in order to render surfaces thereof hydrophilic and dye receptive without impairing the smoothness or optical properties, such as transparency, of the treated article. U.S. Patent No. 2,604,461 (Roth) discloses sulfonating thin film of polystyrene throughout the body of the film to produce a soft gel which has decreased tensile strength and is water-swellable. U.S. Patent No. 2,727,831 (Dixon et al) discloses sulfonating surfaces of polystyrene to form on the surface a slimy mixture which is then treated with an alkali to eliminate the slimy texture and render the surface static free. U.S. Patent No. 2,446,536 (Hardy) discloses treating the surface of copolymers

of styrene and olefins, such as isobutylene, isoprene and butadiene, with fuming sulfuric acid to modify surface characteristics such as tackiness and oil solubility. British Patent No. 1,079,251 discloses treating plastics such as copolymers of styrene and acrylonitrile, copolymers of acrylonitrile, butadiene, and styrene, polystyrene, and acrylic polymers, with a strong aqueous solution of sulfuric acid and chromic acid and then sensitizing the resulting hydrophilic surface to permit deposition of a catalytic film. None of these prior art references disclose treating a normally hydrophobic polymer, such as a copolymer of styrene and acrylonitrile, or body insertion devices or instruments made therefrom, with fuming sulfuric acid to render surfaces thereof durably slippery when wet with water.

The present invention provides an article including at least one part formed from a water insoluble solid copolymer of a vinyl or alpha-methyl vinyl aromatic compound and at least one copolymerizable acyclic vinyl or alpha-methyl vinyl compound, which part has at least one surface which is slippery when in contact with water.

Shaped articles of normally hydrophobic, water-insoluble solid polymers according to the invention, such as copolymers of styrene with copolymerizable acyclic vinyl monomers, e.g. acrylonitrile, are preferably treated with fuming sulfuric acid, to render at least one surface or a portion thereof hydrophilic and durably slippery when wet with water. The conditions of treatment are such that the treated surface retains such properties upon storage, requiring only the application of a film of water to make the surface self-lubricating. Articles made with such surfaces can be repeatedly used after they become dry or dehydrated by merely rewetting, washing and drying after use, and repeated use does not impair the slippery nature of the surface. In short, the treated surface of the article is durable. Such normally hydrophobic polymers can be fabricated in the shape of a body insertion device or instrument, such as those having a curved or rounded outer surface, which surfaces thereof would normally come into contact with the walls, tissue, or members of body orifices or cavities. Such devices are treated in accordance with this invention with fuming sulfuric acid to modify such surfaces, rendering them hydrophilic and durably slippery when wet with water. Such modified devices or instruments can be used without requiring the application of an extraneous lubricant, such as petroleum jelly, and the disadvantages mentioned above which are attendant the use of such lubricant are materially or completely overcome by this invention.

The polymers used in this invention are preferably water-insoluble, hydrophobic solid polymers. The vinyl or alpha-methyl vinyl aromatic monomers can be represented by the structure $Ar—C(R)=CH_2$, where R is hydrogen or methyl and Ar is an aromatic nucleus, preferably of the benzene series. The copolymerizable vinyl or alpha-methyl vinyl compounds have the characteristic group $CH_2=C(R^1)—$, where R^1 is methyl or, preferably, a hydrogen atom. Representative vinyl or alpha-methyl vinyl aromatics which can be used to prepare these copolymers are styrene, alpha-methyl styrene, mono- and di-substituted halostyrenes such as 2,5-dichlorostyrene, vinyl toluene, and the like. Vinyl aromatics which are unsubstituted in the para position are preferred since copolymers thereof, when treated in accordance with this invention to provide the best durable slippery surfaces, have been found upon infrared analysis to have sulfonic acid substitution in the para position.

Preferred representative acyclic vinyl comonomers which are copolymerized with the vinyl aromatic to provide the copolymers used in this invention include those of the general formula $CH_2=C(R^1)—X$, where R^1 is methyl or, preferably, a hydrogen atom and X is —CN, —COOH, and $—COOR^{11}$, where R^{11} is an alkyl with 1 to 8 carbon atoms which can have a hydroxy substituent, comonomers falling within the scope of this latter formula including acrylonitrile, methacrylonitrile, and acrylic and methacrylic acids and alkanol or hydroxy-substituted alkanol esters of such acids, such as butyl acrylate, methyl methacrylate and the like. Other comonomers which can be copolymerized with styrene, or with styrene and comonomers of said general formula $CH_2=C(R^1)—X$, are mono-olefins, such as isobutylene and propylene, and di-olefins, such as isoprene and butadiene, these olefins preferably having 3 to 5 carbon atoms. We have found that copolymers of styrene and acrylonitrile, styrene and n-butylacrylate, styrene, 1,3-butadiene, and acrylonitrile, and styrene and methyl methacrylate are particularly suitable in the practice of this invention.

The relative weight ratio of vinyl aromatic to copolymerizable acyclic vinyl compound in these polymers can vary, but sufficient vinyl aromatic should be used so that the subsequently treated surface of the polymer has a durable hydrophilic, slippery surface, too much vinyl aromatic monomer resulting in a surface which, though it may be hydrophilic, is in the nature of a slime or gel which is not durable and is strongly bonded to the substrate, and is easily washed off or abraded. Generally, the amount of vinyl aromatic in the copolymer should be 20 to 85 weight percent, prefer-

ably 50 to 75 weight percent, and the amount of vinyl comonomer should be 80 to 15 weight percent, preferably 50 to 25 weight percent, these weight percents being conventionally expressed in terms of polymerization charge weights. Where the above-described olefins are used as comonomers in addition to those of the general formula $CH_2=C(R^1)—X$, such olefins will generally amount to 1 to 40 weight percent of the total comonomers copolymerized with the vinyl aromatic (e.g., styrene).

There are many commercially available polymers which can be used in the practice of this invention, such as "Tyril" 760 and 767, which are copolymers of styrene and acrylonitrile, "Neo-Cryl" and "Zerlon", which are copolymers of styrene and methylmethacrylate, "Parapol" S-50, which is a copolymer of styrene and isobutylene, and "Tybrene" 217 and "Cycolac", which are copolymers of blends of copolymers of acrylonitrile, butadiene, and styrene. The copolymers used in this invention can be prepared by any of the known methods of copolymerization, such as emulsion, suspension, solution, or bulk polymerization. The copolymers used in this invention are preferably random copolymers but it is within the scope of this invention to use block or graft copolymers; also, it is within the scope of this invention to use blends of two or more of such copolymers. Thermoplastic polymers are presently preferred in the practice of this invention.

The shaped articles which are treated in accordance with this invention can be in such unfabricated solid form as chips and pellets, or can be fabricated by extrusion, injection or compression molding, machining, calendering, wet- and dry-spinning, potting, casting, and the like, into such fabricated forms as fibers, filaments, yarns, threads, ribbons, tapes, rods, foils, self-supporting films and sheets, moldings, and the like. Preferably, the polymeric material is treated in accordance with this invention in the shape which it will subsequently be used. The polymer material may have incorporated in it various additives and adjuncts such as pigments, dyes and plasticizers, as long as these do not prevent the formation of or adversely affect the hydrophilic slippery surface.

The treatment of the above-described polymers or articles made therefrom, e.g., the body insertion devices, is carried out by contacting one or more desired surfaces of the polymer article, or portions thereof, with fuming sulfuric acid of sufficient concentration for a sufficient period of time and at a sufficient temperature to cause the formation of a durable hydrophilic surface which is slippery when wet with water. The treatment is more than superficial and in most cases visibly affects the appearance of the treated surface. In the case of copolymers which normally are transparent, upon treatment, the degree of transparency is decreased, the treated surface of some copolymers becoming translucent, opaque, etched, or cloudy. The degree or extent of modification of the surface will vary with not only the particular polymer being treated but with the concentrations of the fuming sulfuric acid, and the temperature and duration of the treatment. Simple routine tests can be performed to determine the optimum conditions necessary to provide an article with a durable slippery surface. In any event, it is only the surface of the article which is modified, that is, the article is not sulfonated throughout its interior or bulk, and thus the physical properties, such as tensile strength, generally remain intact and are not materially modified. Generally, a durable slippery surface will be produced at temperatures in the range of 0 to 100°C., preferably 15 to 55°C. and typically at ambient temperature. The duration of the treatment will generally vary from a few seconds to 15 minutes or longer, and contact or treatment times in the range of 30 seconds to 2 minutes generally will be adequate and are preferred.

The fuming sulfuric acid can have 2 to 30 weight percent, preferably 5 to 10 weight percent, free or excess sulfur trioxide. Hot, concentrated sulfuric acid can also be used since it in a sense will be equivalent to fuming sulfuric acid, though the latter is preferred because it will function well without having to be heated. Other chemicals often conventionally referred to as sulfonating agents, such as concentrated sulfuric acid (at room temperature), sulfur trioxide, and chlorosulfonic acid, have not been found suitable to achieve a durable slippery surface.

Contacting of the surface of the polymer article is preferably carried out by immersing the desired surface to be treated in fuming sulfuric acid at room temperature. However, it is also within the scope of this invention to spray the sulfonating agent onto the desired surface to be treated. Following contact of the surface with the sulfonating agent, the treated surface can be drained and washed with water and dried in air. Alternatively, after the water wash, the treated surface can be contacted with a dilute aqueous solution of a base such as ammonium hydroxide, sodium hydroxide, calcium hydroxide, sodium bicarbonate, or potassium carbonate, in order to neutralize any acid groups in the surface or any free acid present on the surface, and the neutralized surface then washed in water and dried in air.

The depth of the treated surface (dry) will vary with the particular polymer material and the treating conditions used and generally will be 2 to 150 microns, though we have found that articles with treated surface of 2 to 70 microns sufficiently exhibit the durable slippery property when wet with water. The treated surface is not only hydrophilic but swells as much as 3 to 4 times in thickness in contact with water, water forming a uniform film on the treated surface. Generally, we have found that surfaces with adequate durable slippery character will have coefficients of friction of .05 or .04 or less, when tested by the ASTM-D-1894-63 test described in Example 2 herein. These durable slippery surfaces will have 20 to 400 milliequivalents per square meter (meq/m^2) of titratable groups with a standard deviation of 7 to 10%. In addition to characterizing the treated surface in these terms of coefficient of friction and titrated groups, its slippery character, when wet with water, can be characterized by likening it to the sliding feeling to the touch imparted by a wet bar of soap or melting ice. Infrared spectral analysis, with a Perkin-Elmer 137 Spectrophotometer, of the treated surface, after being washed, neutralized, and dried in air, reveal the presence of sulfonic acid groups located in the para position on the aromatic nucleous and an absorption band in the hydroxyl region of 2.8 microns. Repeated washing and drying of the treated surface does not alter the slippery character of the surface, nor does mild abrasion or rubbing with a cloth, the treated surface being firmly affixed to the substrate. This surface when dried, does not feel slippery to the touch to any extent, any more than the untreated surface, until wet with water. The material comprising the slippery layer is highly hydrophilic and water-swellable, as contrasted to the hydrophobic substrate to which it is bound. By virtue of the permanent bonding to this substrate, this hydrophilic layer is in effect water-insoluble. It is also resistant to solvents such as benzene, methyl ethyl ketone and chloroform but liquid permeable. Pellets of a 75 weight percent styrene-25 weight percent acrylonitrile copolymer, for example, when treated in accordance with this invention and allowed to soak in chloroform or ethyl acetate, became hollow shells.

The polymer articles, treated in accordance with this invention to impart at least one slippery surface thereto, can be used in a host of applications where the slippery property is of advantage or necessary. Such treated articles in the form of powder, beads, or pellets can be used as a substitute for snow to provide a skiing surface. Contact rollers having a hydrophilic surface can be used in the dispensing of aqueous printing inks, dyes, dopes, adhesives, dust, powders, and many other types of coatings. The hulls of boats can be made of or clad with polymers treated in accordance with this invention since the slippery surface thereof will be less prone to attack or fouling by marine life, fungi, barnacles, microorganisms and the like. Articles which normally wear out and often need to be lubricated with an oil, etc., can be fabricated and have selective surfaces thereof treated in accordance with this invention, the mere wetting of such surfaces with water being sufficient to lubricate the desired surfaces and prevent or minimize wear, such articles including pipes and hose fittings, valves, and nozzles for handling water and water solutions and slurries. Medical devices inserted in body orifices and cavities for purposes of diagnosis or insertion of fluids can be made from plastics having surfaces treated in accordance with this application, the use of such devices made in this fashion making it unnecessary to apply lubricant to the device prior to insertion into the body. Such medical devices include enema tubes, catheters, proctoscopes, specula, receptoscopes, sheaths, ureathal sounds, nasogastric tubes, endotracheal tubes, pessaries, anoscopes, sigmaorthoscopes, retractors, dialators, cystoscopes, and the like, the mere application of water to the treated surface of such articles making the same slippery and readily inserted without the need of a conventional lubricant. Also, diagnostic devices such as fiber optic viewing bundles, temperature or pressure sensing probes, radiopaque diagnostic material, and the like, can be carried or disposed within a body insertable sheath made of such copolymers, the surfaces of the sheath having been treated as described above to render them durably slippery when wet with water. Various other devices and instruments which can be made in accordance with this invention will be apparent to those skilled in the art.

In the accompanying drawing, Figures 1 and 2 illustrate embodiments of a syringe useful, for example, for injecting a medicinal preparation, such as an enema preparation, into a body orifice or cavity. In Figure 1 reference 1 designates a flexible hand-pump or bag made of rubber or the like which is connected to a nozzle or applicator tip 2 the outer surface of at least the terminal portion 3 of which has been treated with fuming sulfuric acid to render it hydrophilic and slippery when wet with water. In Figure 2, reference 6 designates a container, such as a thin-walled polyethylene bottle which is flexible and can be squeezed to expel its contents. Affixed to the threaded neck 7 of the bottle is a nozzle

8, the outer surface of at least the terminal portion 9 of which has been similarly treated to render the same hydrophilic and slippery when wet with water.

In the embodiments illustrated in the drawing, the nozzles or applicator tips are made or fabricated from the above-described copolymers of a vinyl aromatic, such as a styrene-acrylonitrile copolymer, such copolymer being normally transparent, treated surfaces thereof being shown as shaded in the drawing and indicate visible etching or less transparency.

The invention will be further illustrated by the following examples:

EXAMPLE 1

In this example, 5 g. of a transparent, thermoplastic copolymer of 75 wt. % styrene and 25 wt. % acrylonitrile ("Tyril" 767) in the form of pellets (2 mm in diameter and 4 mm in length) were immersed in a bath of fuming sulfuric acid (20 wt. % free SO_3) at room temperature for 15 min. The treated pellets were removed from the treating bath and quickly immersed in a large bath of water and then withdrawn and washed for 5 min. in running tap water. The pellets were then dried in air and had an opaque, translucent appearance and were not slippery when rolled between the fingers. However, when the pellets were wet with water, they were extremely slippery to the touch and appeared substantially swollen when compared with untreated pellets. The washed pellets were immersed in 28% aqueous ammonia hydroxide and when these wet pellets were examined, they too appeared swollen and slippery to the touch. Examination of the wet treated pellets under a microscope using phase-contrast optics revealed a definite surface layer having a thickness of about 200 microns thick when measured with a grid under the microscope.

EXAMPLE 2

A thermoplastic specimen (5 cm. × 10 cm. × 0.13 cm.) of a copolymer of 75 wt. % styrene and 25 wt. % acrylonitrile ("Tyril" 767) was immersed in fuming sulfuric acid (20 wt. % free SO_3) at room temperature for 2 min. The treated sample was removed from the acid bath and immersed in water to remove excess acid. The surface of the treated sample was scrubbed thoroughly with a soft cloth pad to remove excess acid while immersed in water. The water-washed sample was then tested while wet with water according to ASTM D-1894-63, Coefficient of Friction of Plastic Films. Procedure B (Moving Sled-Horizontal Plane) at a crosshead speed of 12.7 cm. using a water-wet stainless steel beam. The coefficient of friction for the treated surface was found to be 0.01 to 0.02. Reflective infrared spectroscopy of the dried treated surface revealed a high degree of sulfonic acid substitution predominantly attached to the para position of the aromatic nuclei. This treated surface layer was found deeper than the 3 micron penetration of the incident infrared beam used.

EXAMPLE 3

A series of specimens of a copolymer having the same dimensions and compositions as that used in Example 2 were individually immersed in fuming sulfuric acid (20% free SO_3) for various length of time at room temperature and then thoroughly water-washed. The coefficient of friction of the treated samples were measured in the manner described in Example 2. The treated samples were also subsequently dried in a dessicator for one day, sectioned on an ultramicrotome, and the sections examined with an optical microscope using phase-contrast optics to determine the depth of treatment. The results of these examinations are summarized in Table I:

TABLE I

Run	Contact time of sample with acid, sec.	Coeff. of friction of treated surface	Depth of treated, dry surface, microns
1	0 (control)	0.07 —0.11	—
2	1	0.07 —0.09	TSTM*
3	2	0.07 —0.09	TSTM
4	5	0.05 —0.07	TSTM
5	15	0.02 —0.05	TSTM
6	30	0.007—0.02	9
7	60	0.007—0.02	5
8	120	0.004—0.01	13.6

*"TSTM" means "too small to measure".

The data of Table I show that the coefficient of friction and depth of the treated surface is a function of the duration of treatment, the longer the contact time of surface with the sulfonating agent, the greater the reduction in friction and the depth of the treated surface. The surfaces of Runs 2—5 were slippery, but not as slippery as those of Runs 6—8. Similar results were found when a styrene-acrylonitrile-butadiene copolymer ("Cycolac") was treated and examined.

Example 4

A series of copolymers of styrene and acrylonitrile were prepared according to the following basic recipe;

TABLE II

Distilled water	150 g.
Sodium lauryl sulfate ...	1.5 g.
Potassium persulfate ...	0.45 g.
Styrene	1.0—X* g. moles
Acrylonitrile	X* g. moles

*X varies from 0.1 to 0.9 and the total amount of monomer varied from 50 to 100 g.

The polymerization reactions were run 20 hrs. at 60°C. The resulting latices were freeze-coagulated and washed with water. The coagulated copolymer was hot pressed and cut into 7.6 cm. diameter samples approximately 0.13 cm. thick and each treated with fuming sulfuric acid for 5 to 15 min. in the manner described in Example 1. The nature of the treated surface when wet with water and examined by touch was determined, the results being summarized in Table III.

TABLE III

Run	Amt. of styrene wt. % Charged	Amt. of styrene wt. % Found (anal)	Nature of treated surface*
1	0	0	not slippery
2	20	22.5	not slippery
3	30	35	not slippery
4	40	47.5	not slippery
5	50	58.5	slightly slippery
6	60	67.4	slippery
7	70	82.2	slippery
8	80	89.0	slippery
9	90	94.3	slightly slippery
10	100	100	not slippery

*Though samples in each run were contacted 5 and 15 min. with fuming sulfuric acid, these different contact times did not appear to give different results.

Another series of polymerizations were carried out in which styrene-n-butyl acrylate copolymers of varying weight ratios of monomers were prepared and treated with fuming sulfuric acid. In each polymerization, an ampoule was charged with a solution of 1.0 g. sodium lauryl sulfate and 0.2 g. of potassium persulfate, and then with the monomers. The charged ampoules were sealed and the polymerizations were run 20 hrs. at 60°C. in a tumbler bath. The latices were freeze-coagulated, washed and dried. The products were then pressed into film specimens (5 cm. × 10 cm. × 0.13 cm.) and treated with fuming sulfuric acid (10 wt. % free SO_3) at 25°C. for 1 min., then water-washed. The treated surfaces of all specimens were slippery when wet with water and their coefficients of friction were measured in accordance with the above-described procedure. Results are set forth in Table IV.

TABLE IV

Run	Amt. of Styrene wt. % Charged	Amt. of Styrene wt. % Found (anal.)	Coeff. of friction of treated surface
1	70	64.8	0.01—0.02
2	60	55.8	0.01—0.02
3	50	—	0.01—0.02
4	40	38.0	0.01—0.02
5	30	26.0	0.02—0.03

The above data reveal not only that it is essential to use a copolymer in order to obtain the desired slippery surface, but that a sufficient amount of the styrene monomer must be used in preparing the copolymer in order to obtain a slippery surface, though said amount will vary with the copolymer used.

EXAMPLE 5

In this example, a series of 15 g. samples of pellets (having a surface area of about 8 m^2/kg.) of a copolymer of 75 wt. % styrene and 25 wt. % acrylonitrile ("Tyril" 767) were immersed and stirred in fuming sulfuric acid (2 wt. % free SO_3) for 2 min. at 30°C. After such treatment, the pellets were removed from the bath and quenched and washed in a bath of tap water, then washed for 5 min. in running tap water, neutralized by shaking in 5% aqueous sodium bicarbonate for 10 min., then rewashed in running tap water for 5 min. The pellets were then column washed slowly with 12% aqueous hydrochloric acid (to convert hydrophilic groups to acid groups), then washed with deionized water until all traces of hydrochloric acid were removed, and then titrated with standard base to a light pink phenolphthalein endpoint to ascertain the hydroprilic groups present. In all, eight samples were thus prepared and evaluated and the mean amount of hydrophilic groups was found to be 86.0 meq/m^2, the standard deviation being 7%.

EXAMPLE 6

A film of a copolymer of acrylonitrile, butadiene and styrene ("Cycolac") was prepared by compression molding pellets of said copolymer. The film was immersed in fuming sulfuric acid (5 wt. % free SO_3) for 4 min, at room temperature. The treated film was then washed thoroughly in water and the wet treated surface was found to be very slippery. The film was then immersed briefly in 5 wt. % aqueous sodium bicarbonate and again rinsed with water. The so-treated wet surface had the same slippery feel. A finite boundary was observed between the treated and untreated portion of the film; by running the finger over the film, a definite ridge could be detected at the boundary line between the treated and untreated surface of the film due to the swollen nature of the treated surface. Water filmed out on the treated area but beaded on the untreated area of the surface.

EXAMPLE 7

Pellets of a copolymer of acrylonitrile, butadiene and styrene ("Tybrene" 217) were melted and molded to form an enema tube about 7.5 cm. in length with an outside diameter of 0.8 cm. The tube was immersed in a bath of fuming sulfuric acid (7 wt. % free SO_3) to a depth of 4.5 cm. for 4 min. at 135°C. The tube was then washed in water for 5 min. in running tap water, immersed in a bath of 5 wt. % aqueous ammonia for 10 min. with shaking, and rewashed for 5 min. in running tap water. The portion of the tube that was contacted with the sulfonating agent appeared opaque and translucent, whereas the untreated portion of the tube was clear and transparent. When wet with water, the treated surface of the tube appeared far more slippery than the untreated portion.

EXAMPLE 8

Pellets of a thermoplastic copolymer of 75 wt. % styrene and 25 wt. % acrylonitrile ("Tyril" 767) were melted and injection molded to form an enema tube having a length of 9 cm., an outside diameter of 0.8 cm. and an inside diameter of 0.6 cm. The tube was immersed to a depth of 4.5 cm. in fuming sulfuric acid (2 wt. % free SO_3) for 2 min. at 35°C. The treated tubes were quickly quenched in an excess of tap water, washed in running tap water for 5 min., neutralized in 5 wt. % aqueous sodium bicarbonate for 10 min. with shaking, and rewashed in tap water for 5 min. The portion of the tube that was contacted with the sulfonating agent appeared opaque and translucent, whereas the untreated portion of the tube was clear and transparent. When wet with water, the treated surface of the tube appeared far more slippery than the untreated portion.

EXAMPLE 9

A strip (5 cm. × 10 cm. × 0.13 cm.) of a flexible rubbery copolymer of 30 mole % styrene and 70 mole % n-butylacrylate was immersed in fuming sulfuric acid (4 wt. % free SO_3) at room temperature for one minute. The treated strip was then washed in water and its coefficient of friction was measured, using the procedure described in Example 3, and found to be 0.02 to 0.03. The treated surface of the strip was opaque and durably slippery when wet with water and its flexibility and rubbery nature was not detectably changed by the treatment.

EXAMPLE 10

A strip of a copolymer of 50 wt. % styrene and 50 wt. % n-butylacrylate was immersed in fuming sulfuric acid (4 wt. % free SO_3) for 2 min. at 28°C. and washed, and neutralized according to the procedure described in Example 4. The treated surface of the film was found to be slippery when wet with water and it had a coefficient of friction of 0.02 when tested by the procedure of Example 3.

EXAMPLE 11

A molded strip (5 cm. × 10 cm. × 0.13 cm.) of a copolymer of 50 wt. % styrene and 50 wt. % methylmethacrylate was immersed in fuming sulfuric acid (10 wt. % free SO_3) at room temperature for 2 min. The sample was washed in water and its coefficient of friction was determined by the procedure described in Example 3 and found to be 0.02 to 0.03), the treated surface being slippery when wet with water.

EXAMPLE 12

A film of flexible copolymer of 50 wt. % styrene and 50 wt. % isobutylene was immersed in fuming sulfuric acid (20 wt. % free SO_3) for 30 min. at ambient temperature. The treated film was washed in water and was slippery when wet with water and had a coefficient of friction of 0.05 when tested by the procedure of Example 3.

Comparative Example

For purposes of comparison, the surfaces of a number of different polymers were contacted with sulfonating agents and found to produce treated surfaces which did not have durable slippery surfaces. For example, polystyrene when contacted with fuming sulfuric acid (20 wt. % free SO_3) at 80°C. produced a treated surface having a nature of a slimy gel which sluffed off when gently rubbed or washed in water, and the exposed polystyrene substrate did not have a slippery nature when wet with water though it was hydrophilic. Polystyrene when immersed in fuming sulfuric acid (5 wt. % free SO_3) at room temperature or in concentrated sulfuric acid at room temperature and at temperatures up to 74°C., did not become slippery when wet with water. Further, the surface imparted to polystyrene when treated with fuming sulfuric acid (5 wt. % free SO_3) at temperatures of 70 to 85°C. could be easily rubbed off with the finger. A copolymer of 70 wt. % styrene and 30 wt. % butadiene ("Pliolite" S7) when treated 1 min. with fuming sulfuric acid (20 wt. % free SO_3) at 25°C. developed a loose gel which was easily removed from the treated surface. A vinyl benzoate-butylacrylate copolymer, when treated for 2 min. with fuming sulfuric acid (20 wt. % free SO_3) at room temperature, produced a hydrophilic surface but it wasn't slippery when wet with water.

The words "Tyril", "Neo-Cryl", "Zerlon", "Tybrene", "Cycolac", and "Pliolite", as used herein are Registered Trade Marks.

WHAT WE CLAIM IS:—

1. An article including at least one part formed from a water insoluble solid copolymer of a vinyl or alpha-methyl vinyl aromatic compound and at least one copolymerizable acyclic vinyl or alpha-methyl vinyl compound, which part has at least one surface which is slippery when in contact with water.

2. An article according to claim 1 wherein the surface has been contacted with fuming sulphuric acid whereby the surface swells in contact with the water and is slippery.

3. An article according to claim 1 or claim 2 formed from styrene and at least one comonomer of the formula $CH_2=C(R^1)-X$, where R^1 is methyl or a hydrogen atom, and X is —CN, —COOH, or —COOR^1, where R^1 is an alkyl having 1 to 8 carbon atoms.

4. An article according to any preceding claim in which the copolymer comprises 20—85 weight percent styrene and 80—15 weight percent comonomer.

5. An article according to claim 4, in which the copolymer comprises 50—75 weight percent styrene and 50—25 weight percent comonomer.

6. An article according to claim 4 or claim 5, in which the copolymer is styrene-acrylonitrile copolymer, an acrylonitrile, butadiene, styrene copolymer, a styrene-butylacrylate copolymer, a styrene-methylmethacrylate copolymer, or a styrene-isobutylene copolymer.

7. An article according to any preceding claim in which the treated surface has a coefficient of friction of less than 0.05, when in contact with water.

8. An article according to any preced-

ing claim, in which the treated surface has a depth of 2 to 70 microns.

9. An article according to any preceding claim wholly formed from the copolymer.

10. An article according to any preceding claim comprising an enema tube.

11. A process for rendering the surface or part of the surface of an article according to any preceding claim slippery when contacted with water, comprising treating the surface or part of the surface with fuming sulphuric acid.

12. A process according to claim 11 in which the conditions of treatment of the surface are sufficient to render said treated surface 2—70 microns thick and impart to it a coefficient of friction of 0.05 or less, when in contact with water.

13. An article according to claim 1 substantially as herein described with reference to the accompanying drawings.

14. An article according to claim 1 substantially as herein described with reference to any one of the examples.

15. A process for providing a polymer article with a surface which is hydrophilic and slippery when in contact with water substantially as herein described.

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1280349 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 1

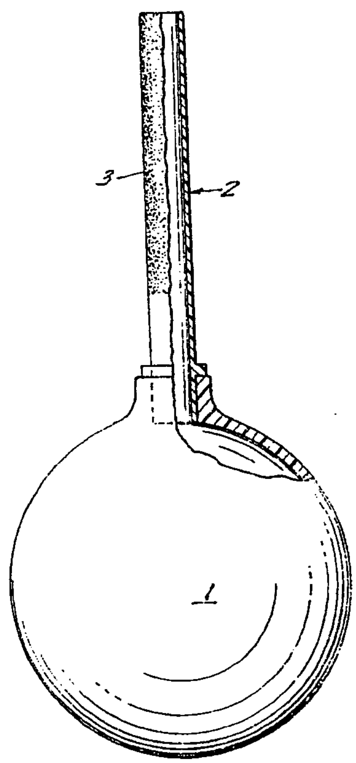

FIG. 2